THE ADDITION OF THE GRIGNARD REAGENT TO HINDERED *ALPHA, BETA*-UNSATURATED KETONES

BY

JOHN SAWYERS MEEK

A. B., University of Wisconsin, 1941

M. S., University of Illinois, 1944

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The Grignard reagent may condense with an α, β-unsaturated ketone in either the 1, 2- or the 1, 4-manner. The way in which it does so is determined largely by the spatial and chemical nature of the groups in the molecule. An example of the effect of the spatial nature of a group is to be found in the mesityl ketones. These ketones because of two *ortho* methyl substituents have an extremely hindered carbonyl group, and only recently has the 1, 2-addition of the Grignard reagent to a mesityl ketone been accomplished. [1 2 3] So far all known mesitoylethylenes tried have been found to condense with the Grignard reagent in the 1, 4-manner and none has been found to undergo 1, 2-addition. However, it seemed possible that a mesitoylethylene could be prepared with sufficient hindrance in the *beta* position to prevent 1, 4-addition, and then the ketone would combine with the Grignard reagent in the 1, 2-manner. To test this possibility it was decided to synthesize β-phenylmesitalacetomesitylene (I) and β-mesitylmesitalacetomesitylene (II). Both of these would possess more *beta* hindrance than any previously prepared mesitoylethylene.

An example of the chemical effect in the addition of the Grignard reagent is to be found in α, β-acetylenic ketones. These combine with the Grignard reagent in the 1, 2-manner, and in no case has the 1, 4-addition of the Grignard reagent to such a ketone been reported in the literature. However, it seemed possible that there would be sufficient hindrance in mesitoylphenylacetylene (III) to prevent 1, 2-addition, and that 1, 4-addition might occur instead. With mesitoylmesitylacetylene (IV) it was thought that the chemical effect of the acetylenic group and the *beta* hindrance of a mesityl group would cause 1, 2-addition of the Grignard reagent to this new type of ketone.

Discussion and Experimental

Mesitalacetomesitylene (V) has been reported to condense with methylmagnesium iodide to give an oil to which was assigned the structure of β-mesitylbutyromesitylene. Since the structure of this compound had not been proven and since the addition of the appropriate Grignard reagent to mesitalacetomesitylene would lead to a

method of preparing I and II, the interaction between V and the Grignard reagent was investigated further.

The condensation product of methylmagnesium iodide with V and that of mesitylmagnesium bromide with mesityl propenyl ketone, when decomposed under ordinary conditions, gave the same white solid, β-mesitylbutyromesitylene (VI). which melted at 44-45°. The decomposition of either of the condensation products with hydrochloric acid at zero degrees gave the enol form of VI, which was converted into two isomers of 1,3-dimesityl-1-buten-1-peroxide, melting at 95° and 119°.

The condensation product of phenylmagnesium bromide with mesitalacetomesitylene when decomposed with bromine gave two isomeric forms of α-bromo-β-mesityl-β-phenylpropiomesitylene. One melted at 150 ° and, when dehydrobrominated with ethanolic potassium hydroxide, gave an isomer of β-phenylmesitalacetomesitylene (I) which melted at 100°. The other α-bromoketone melted at 139-141° and gave rise to the other isomer of I, melting at 121°. The condensation product of phenylmagnesium bromide and V when decomposed gave β-mesityl-β-phenylpropiomesitylene, melting at 92°. This ketone was prepared also from mesitylmagnesium bromide and benzalacetomesitylene.

The condensation product of mesitylmagnesium bromide with V when decomposed with a saturated solution of ammonium chloride gave β, β-dimesitylpropiomesitylene (m. p. 100°); when decomposed with bromine it gave α-bromo-β, β-dimesitylpropriomesitylene. This when dehydrobrominated, gave β-mesitylmesitalacetomesitylene (II); m.p. 156°. This highly hindered ketone was found to be inert to methylmagnesium iodide under ordinary conditions, while the higher-melting isomer of I appeared to condense to some extent with this Grignard reagent. Neither I nor II was reduced by hydrogen and the Adams catalyst under ordinary conditions. Even when allowed to stand for five days in alkaline hydrogen peroxide, II was not converted to an oxido derivative.

Mesitoylphenylacetylene (III) and mesitoylmesitylacetylene (IV) were prepared from mesitoyl chloride and the corresponding sodium

acetylides. Both were found to condense with methyl, phenyl, and mesityl Grignard reagents in the 1, 4-manner. The condensation of III with mesitylmagnesium bromide and the condensation of IV with phenylmagnesium bromide gave the higher-melting isomer of I, none of the lower-melting isomer being obtained in this manner. The condensation of IV and methylmagnesium iodide produced an isomer of β-methylmesitalacetomesitylene; m.p. 103°. This ketone was converted into a second isomer by treatment with acid or base, m.p. 78°.

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Vita

The writer was born in Madison, Wisconsin, August 12, 1918. He attended the elementary schools in that city, and graduated from the University of Wisconsin with a Bachelor of Arts degree in 1941. In the fall of 1941, he entered the Graduate School of the University of Illinois. He held a teaching assistantship in Chemistry during 1941-1943 and a University fellowship during 1943-1944. He received a Master of Science degree in Chemistry in 1944. In the year 1944-1945 he held the Allied Chemical and Dye Corporation fellowship.

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